

The thermodynamic entropy of a macroscopic quantum system is a continuous function of energy

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Abstract

The proper definition of entropy is fundamental to the relationship between statistical mechanics and thermodynamics. It also plays a major role in the recent debate about the validity of the concept of negative temperature. In this paper, I analyze and calculate the thermodynamic entropy for large, but finite quantum mechanical systems. A special feature of this analysis is that the thermodynamic energy of a quantum system is shown to be a continuous variable, rather than being associated with discrete energy eigenvalues. Calculations of the entropy as a function of energy can be carried out with a Legendre transform of thermodynamic potentials obtained from a canonical ensemble. The resultant expressions for the entropy are also able to describe equilibrium between quantum systems having incommensurate energy-level spacings. This definition of entropy preserves all required thermodynamic properties, including satisfaction of all postulates and laws of thermodynamics. It also demonstrates the consistency of the concept of negative temperature with the principles of thermodynamics.

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I. INTRODUCTION

In recent years, there has been a renewal of interest in the fundamental definition of the thermodynamic entropy in statistical mechanics. An important source of that interest has been the controversial claims that the Gibbs “volume” entropy (defined below) is the only valid definition[1–6], and that the concept of negative temperature is inconsistent with thermodynamics[7–15]. Earlier work on classical systems has shown how a valid definition of entropy is consistent with negative temperatures, giving correct thermodynamic predictions when the volume entropy does not[16–23].

The entropy of quantum systems is complicated by a discrete energy spectrum, which has led many to regard the entropy as being defined only at energies corresponding to eigenstates[24, 25], or as constants between eigenvalue energies (step functions)[4–6]. In this paper, I argue that the thermodynamic energy of macroscopic quantum systems has a continuous spectrum of values, even though the eigenvalues of the energy form a discrete set. To briefly summarize my arguments, macroscopic measurements never put a many-body system into an energy eigenstate. The small interactions that are necessary to establish thermodynamic equilibrium between two or more systems are sufficient to alter the discrete energy spectra of the isolated systems. This means that the projection of an eigenstate of the composite system of interacting subsystems onto the energy levels of an isolated subsystem will never produce an eigenstate of the isolated subsystem. An isolated system will necessarily be described by an ensemble of quantum states, including contributions from many energy eigenvalues.

I begin by demonstrating in Section II that the thermodynamic energy of an isolated quantum system that was previously in thermal contact with another system is a continuous variable. Section III reviews the canonical probability distribution of energy in a system that has been in contact with a thermal reservoir, that is, with a very large (formally, infinite) system. I analyze the canonical distribution in terms of a Massieu function[26, 27], in order to be able to carry out calculations for either a monotonic or a non-monotonic energy density of states. The essential features of an ensemble for an isolated system are then shown to depend on an internal temperature variable, which leads to a method for calculating the entropy of a macroscopic quantum system. As examples, explicit expressions are derived for the entropy of quantum simple harmonic oscillators and two-level objects. The entropy of a system of two-level objects has a non-monotonic density of states, and serves to demonstrate

that negative temperatures are consistent with the principles of both quantum statistical mechanics and thermodynamics, as previously shown for the classical case in Ref. 23.

II. THERMODYNAMIC ENERGY IN QUANTUM SYSTEMS

To see the unique way in which interactions affect thermal ensembles in quantum statistical mechanics and lead to the thermodynamic energy being a continuous function, consider a composite system with M macroscopic (many-body) subsystems. The macroscopic observables for the composite system are just the set of $3M$ variables $\{\mathbf{E}, \mathbf{V}, \mathbf{N}\} = \{E_j, V_j, N_j | j = 1, \dots, M\}$, where \mathbf{E}, \mathbf{V} , and \mathbf{N} denote the sets of energy, volume, and particle numbers. To reduce the proliferation of subscripts, the equations are written for a single type of particle, but the generalization to many types of particles is obvious. For quantum spins, the magnetization will also be included in the macroscopic variables.

Each macroscopic subsystem j will be characterized by a Hamiltonian H_j , *when it is isolated from other subsystems*. To establish thermal equilibrium between subsystems, direct interactions between particles in different subsystems are necessary. These additional interactions will be denoted by the interaction Hamiltonians $\mathbf{L} = \{L_{j,k} | j = 1, \dots, M-1; k = j, \dots, M; \}$. These interactions between macroscopic subsystems prove to be essential in deriving the quantum entropy.

The extension of the definition of entropy to quantum systems follows the basic pattern of considering thermodynamic interactions between subsystems of a composite system that I discussed for classical composite systems in earlier work[21]. However, there are some subtleties associated with the discreteness of the spectrum of energy eigenvalues for finite systems. In particular, the effects of interactions between subsystems, denoted by \mathbf{L} , must be treated carefully. I begin by introducing a fairly standard notation for quantum states and equilibrium quantum ensembles, first for isolated subsystems, and then for interacting subsystems.

II.1. Isolated quantum subsystems

First consider the case in which $\mathbf{L} = 0$, so that every macroscopic subsystem is isolated. Denote the quantum Hamiltonian for the j -th subsystem by H_j , and the corresponding

quantum numbers by ν_j . The energy eigenvalue equation is then

$$H_j|\nu_j\rangle = \epsilon_j(\nu_j)|\nu_j\rangle, \quad (1)$$

where $|\nu_j\rangle$ denotes an eigenstate. I assume that for each subsystem j , the set of $|\nu_j\rangle$ form a complete, orthonormal set.

A general quantum state of subsystem j will be denoted by $|\psi_j\rangle$. It can be expanded in the eigenstates of the subsystem,

$$|\psi_j\rangle = \sum_{\nu_j} c_{\nu_j} |\nu_j\rangle, \quad (2)$$

where the c_{ν_j} 's are complex numbers, $c_{\nu_j} = |c_{\nu_j}| \exp(i\phi_{\nu_j})$.

$$c_{\nu_j} = \langle \nu_j | \psi_j \rangle \quad (3)$$

If $|\psi_j\rangle$ is properly normalized, we have

$$\sum_{\nu_j} |c_{\nu_j}|^2 = 1. \quad (4)$$

Assuming that there is a probability distribution, $P_j(\psi_j)$, defined on the set of quantum states, then the average of an arbitrary operator A will be given by

$$\langle\langle A \rangle\rangle = \sum_{\psi_j} P_j(\psi_j) \langle \psi_j | A | \psi_j \rangle, \quad (5)$$

where the double angular brackets indicate that both a quantum expectation value and an ensemble average are being calculated, and the summation symbol is intended to cover whatever sums and integrals are appropriate. Using Eq. (2), $\langle\langle A \rangle\rangle$ can be written as

$$\langle\langle A \rangle\rangle = \sum_{\{c_j\}} \sum_{\mu_j} \sum_{\nu_j} P_j(\{c_j\}) c_{\mu_j}^* c_{\nu_j} \langle \mu_j | A | \nu_j \rangle. \quad (6)$$

where $\{c_j\}$ indicates a set of values of c_{ν_j} corresponding to the quantum state $|\psi_j\rangle$, and the sum over $\{c_j\}$ is the sum over all quantum states in the ensemble.

In equilibrium, all phases, ϕ_j , are equally probable. Integrating over the phases gives a factor of zero for all cross terms, leaving the expression

$$\langle\langle A \rangle\rangle = \sum_{\nu_j} \sum_{\{c_j\}} P_j(\{c\}) |c_{\nu_j}|^2 \langle \nu_j | A | \nu_j \rangle. \quad (7)$$

This expression can be simplified by writing

$$P_j(\nu_j) = \sum_{\{c_j\}} P_j(\{c_j\}) |c_{\nu_j}|^2, \quad (8)$$

so that $P(\nu_j) \geq 0$. This gives

$$\langle\langle A \rangle\rangle = \sum_{\nu_j} P_j(\nu_j) \langle\nu_j|A|\nu_j\rangle. \quad (9)$$

Further noting that $\langle\langle 1 \rangle\rangle = 1$, we see that

$$\sum_{\nu_j} P_j(\nu_j) = 1, \quad (10)$$

so that $P_j(\nu_j)$ acts very much like a probability. Averages over the equilibrium quantum ensemble can be computed as if $P_j(\nu_j)$ were a probability. It is quite common to speak loosely of $P_j(\nu_j)$ as being the probability of the subsystem being in the $|\nu_j\rangle$ eigenstate, but it is well known this is not correct. $P_j(\nu_j)$ is the probability that a precise measurement of the energy would put the subsystem into the $|\nu_j\rangle$ eigenstate. Since a macroscopic subsystem is generally in a state of the form given in Eq. (2), and macroscopic measurements cannot put a subsystem in an eigenstate, the true probability of a real macroscopic subsystem being in an energy eigenstate is zero. This leads to the question of what we do know about the distribution of quantum states in interacting subsystems.

II.2. Interacting quantum subsystems

An important feature of interacting quantum subsystems is that the spectrum of energy eigenvalues is not related to the corresponding spectra for the isolated subsystems in a simple way. The composite subsystem has new eigenfunctions with new eigenvalues that depend on the interactions $\mathbf{L} \neq 0$. As an example, consider two interacting subsystems with the following Hamiltonian.

$$H_{1,2} = H_1 + H_2 + L_{1,2} \quad (11)$$

The eigenvalue equation for this Hamiltonian can be written as

$$H_{1,2}|\nu_{1,2}\rangle = \epsilon_{1,2}(\nu_{1,2})|\nu_{1,2}\rangle, \quad (12)$$

where $|\nu_{1,2}\rangle$ denotes the eigenstate, and $\nu_{1,2}$ the quantum number. The eigenstates $|\nu_{1,2}\rangle$ form a complete, orthonormal set.

A general quantum state of the composite system of interacting subsystems will be denoted by $|\Psi_{1,2}\rangle$. It can be expanded in the eigenstates of the composite system.

$$|\Psi_{1,2}\rangle = \sum_{\nu_{1,2}} C_{\nu_{1,2}} |\nu_{1,2}\rangle, \quad (13)$$

where the $C_{\nu_{1,2}}$'s are complex numbers.

$$C_{\nu_{1,2}} = \langle \nu_{1,2} | \Psi_{1,2} \rangle \quad (14)$$

If $|\Psi_{1,2}\rangle$ is properly normalized, we have

$$\sum_{\nu_{1,2}} |C_{\nu_{1,2}}|^2 = 1. \quad (15)$$

II.3. Energy distribution of an individual subsystem due to interactions

Given the eigenstates and eigenvalues of the composite system of interacting subsystems and the probability distribution $P_{1,2}(\nu_{1,2})$, we can compute the energy distribution in the individual subsystems. If the composite system is in a state $|\Psi_{1,2}\rangle$, the projection onto the eigenstate $|\nu_1\rangle$ of the isolated subsystem 1 is

$$\langle \nu_1 | \Psi_{1,2} \rangle = \sum_{\nu_{1,2}} C_{\nu_{1,2}} \langle \nu_1 | \nu_{1,2} \rangle \quad (16)$$

The expectation of the energy E_1 of subsystem 1, given that the composite system is in state $|\Psi_{1,2}\rangle$, is

$$\begin{aligned} \langle E_1 \rangle_{\Psi_{1,2}} &= \langle \Psi_{1,2} | H_1 | \Psi_{1,2} \rangle \\ &= \sum_{\mu_1} \sum_{\nu_1} \langle \Psi_{1,2} | \mu_1 \rangle \langle \mu_1 | H_1 | \nu_1 \rangle \langle \nu_1 | \Psi_{1,2} \rangle \end{aligned} \quad (17)$$

Because $|\nu_1\rangle$ is an eigenfunction of H_1 , Eq. (17) becomes

$$\langle E_1 \rangle_{\Psi_{1,2}} = \sum_{\nu_1} \langle \Psi_{1,2} | \nu_1 \rangle \langle \nu_1 | H_1 | \nu_1 \rangle \langle \nu_1 | \Psi_{1,2} \rangle \quad (18)$$

or, using Eq. (16),

$$\langle E_1 \rangle_{\Psi_{1,2}} = \sum_{\nu_1} |C_{\nu_{1,2}}|^2 |\langle \nu_1 | \nu_{1,2} \rangle|^2 E_1(\nu_1) \quad (19)$$

Averaging over the probability distribution of the states of the composite system gives

$$\langle \langle E_1 \rangle \rangle = \sum_{\nu_1} E_1(\nu_1) \sum_{\nu_{1,2}} P_{1,2}(\nu_{1,2}) |C_{\nu_{1,2}}|^2 |\langle \nu_1 | \nu_{1,2} \rangle|^2 \quad (20)$$

This can be simplified by defining

$$p_1(\nu_1) = \sum_{\nu_{1,2}} P_{1,2}(\nu_{1,2}) |C_{\nu_{1,2}}|^2 |\langle \nu_1 | \nu_{1,2} \rangle|^2. \quad (21)$$

where $1 \geq p_1(\nu_1) \geq 0$, and $\sum_{\nu_1} p_1(\nu_1) = 1$. This gives

$$\langle \langle E_1 \rangle \rangle = \sum_{\nu_1} E_1(\nu_1) p_1(\nu_1). \quad (22)$$

The value $\langle \langle E_1 \rangle \rangle$, including both quantum expectation values and ensemble averages, corresponds to the thermodynamic energy, U_1 , so that we can also write

$$U_1 = \sum_{\nu_1} E_1(\nu_1) p_1(\nu_1). \quad (23)$$

The most important feature of Eqs. (22) and (23) is that they demonstrate that subsystems that interact within a composite system are not in energy eigenstates. This, in turn, implies that the thermodynamic energy of a quantum subsystem in equilibrium with another quantum subsystem can vary continuously, even though the energy spectra are discrete. U_1 remains a continuous variable when subsystems in thermal equilibrium are separated.

It is appropriate to compare the magnitudes of typical energy spacings with typical thermal fluctuations of the energy. In an example presented below, we will consider a subsystem composed of N two-level quantum objects, with a level spacing of ϵ . Characteristic average energies are of the order of $N\epsilon$, so that the relative size of the level spacing in comparison with the total energy is of the order of $1/N$. In contrast, relative fluctuations of the energy are typically of the order of $1/\sqrt{N}$. For a macroscopic subsystem with $N \approx 10^{20}$, the thermal fluctuations are roughly 10^{10} larger than the energy level spacing.

It is also important that typical energies associated with the interactions \mathbf{L} are expected to scale with the surface area of the subsystem, so that their relative magnitude goes as $N^{-1/3}$. This can easily be larger than the thermal fluctuations, and much larger than the energy-level spacing. As a result, there is nothing to prohibit quantum subsystems with incommensurate energy-level spacings from exchanging energy and being in thermal equilibrium with each other. Indeed, the explicit forms for the entropies of model subsystems that are derived in Section IV can be used to predict thermal behavior due to interactions between macroscopic subsystems with incommensurate energy-level spacings.

Another consequence of Eq. (23) is that the concept of a microcanonical ensemble must be modified in quantum statistical mechanics, as discussed in the next subsection.

II.4. Separated quantum subsystems

When two or more interacting *classical* subsystems are separated and isolated, they will each go into a microscopic state with a unique energy. Naturally, the value of that energy can only be predicted to within the thermal fluctuations of the energy before separation. Nevertheless, it clearly makes sense to describe an isolated classical subsystem by a microcanonical ensemble with an exact value for the energy, regardless of its history.

The situation when *quantum* subsystems are separated is quite different. Each subsystem will go into a quantum state that can be expressed as a linear combination of eigenstates, as shown in Eq. (2). However, Eq. (23) shows this quantum state will not be in an energy eigenstate, so the subsystems cannot be described by the usual microcanonical ensemble with an exact value for the energy. As demonstrated in the next section, it is still possible to compute the fundamental relation, $S_j = S_j(U_j, V_j, N_j)$, for each subsystem by using the canonical ensemble, which is valid for quantum statistical mechanics. Explicit examples of such calculations are then given in Section IV.

III. CALCULATING THE ENTROPY THROUGH THE CANONICAL ENSEMBLE

To determine the average thermodynamic energy we must calculate the “probabilities,” $p_j(\nu_j)$, that were defined in Eq. (21). The simplest way to do this is through the canonical ensemble, which will give us a thermodynamic potential that contains all thermodynamic information for the subsystem of interest.

A Legendre transform will then give the entropy as a function of the thermodynamic energy. Because I am interested in using a formalism that is also valid for subsystems with non-monotonic entropies, I will use a Massieu function to derive the entropy[26, 27]. Since a Massieu function might be somewhat less familiar than the more common Helmholtz free energy, it will be reviewed in the subsection following that on the canonical ensemble.

III.1. Canonical ensemble

If we put the subsystem of interest, which we will pick to be $j = 1$, into equilibrium with a reservoir that has a known continuous density of states, $\omega_R(E_R)$, the value of $p_1(\nu_1)$ will

be determined by the proportionality:

$$p_1(\nu_1) \propto \omega_R(E_T - E_1(\nu_1)), \quad (24)$$

where $E_T = E_R + E_1(\nu_1)$ is the total energy of the reservoir and subsystem 1. Taking the logarithm of each side and expanding ω_R , gives

$$\begin{aligned} \ln p_1(\nu_1) = \ln \omega_R(E_T) - E_1(\nu_1) \left[\frac{\partial}{\partial E_T} \ln \omega_R(E_T) \right] \\ - \ln Z' + \dots, \end{aligned} \quad (25)$$

where Z' is a constant. The higher-order terms that are indicated by the dots in Eq. (25) are proportional to the ratio of E_1 to the much larger values of E_T , and in the limit of an infinite reservoir, they vanish. Although this calculation is based on finding the mode of the probability distribution, rather than the mean, the assumption of an infinite reservoir is sufficient to make the mean and mode agree. Interactions between finite subsystems will be discussed elsewhere, but the effects are proportional to the inverse of the number of particles, and are not measurable for macroscopic subsystems.

Defining

$$\beta = \frac{\partial}{\partial E_T} \ln \omega_R(E_T), \quad (26)$$

Eq. (25) becomes

$$\ln p_1(\nu_1) = \ln \omega_R(E_T) - \beta E_1(\nu_1) - \ln Z', \quad (27)$$

or

$$p_1(\nu_1) = \frac{1}{Z'} \omega_R(E_T) \exp(-\beta E_1(\nu_1)). \quad (28)$$

Since $\omega_R(E_T)$ does not depend on ν_1 , we can simplify the expression by defining a new constant $Z = Z'/\omega_2(E_{1,2})$, which gives

$$p_1(\nu_1) = \frac{1}{Z} \exp(-\beta E_1(\nu_1)). \quad (29)$$

This is, of course, just the canonical distribution for subsystem 1 for an inverse temperature $\beta = 1/k_B T$. The partition function $Z = Z(\beta)$ in Eq. (29) is given by the normalization condition,

$$Z = \sum_{\nu_1} \exp(-\beta E_1(\nu_1)). \quad (30)$$

Note that the only property of the reservoir that enters into this equation is the inverse temperature β , which is the only property of the reservoir needed to determine the thermodynamics of subsystem 1.

The average energy of subsystem 1, which can be identified with the thermodynamic energy, U_1 , is

$$\begin{aligned} U_1(\beta) &= \sum_{\nu_1} E_1(\nu_1) p_1(\nu_1) \\ &= \frac{1}{Z(\beta)} \sum_{\nu_1} E_1(\nu_1) \exp(-\beta E_1(\nu_1)). \end{aligned} \quad (31)$$

III.2. Equilibrium between finite systems

An important concern for practical applications is how the values of $p_1(\nu_1)$ for subsystem 1 in Eq.(29) are affected by replacing the infinite reservoir R , used in Eq. (24), by a finite subsystem 2. The higher-order terms in Eq. (25) no longer vanish, but they are small.

It is not really necessary for Eq.(29) to be valid for all values of $E_1(\nu_1)$. Because the values of $p_1(\nu_1)$ will only be significantly different from zero within the thermal fluctuations δE_1 , it is only necessary for Eq.(29) to be valid over a range of energies of the order of δE_1 . As long as the ratio $\delta E_1/U_2$ is small, Eq.(29) will be accurate. From a consideration of the magnitude of the fluctuations, the condition of validity is that

$$\frac{\delta E_1}{U_2} \approx \sqrt{\frac{N_1}{N_2(N_1 + N_2)}} \ll 1. \quad (32)$$

This condition will be easily satisfied for $N_2 \gg N_1$. For the opposite case of subsystem 1 being in equilibrium with a relatively small subsystem 2, so that $N_2 \ll N_1$, Eq. (32) becomes $\delta E_1/U_2 \approx 1/\sqrt{N_2}$. This condition can also be satisfied if subsystem 2 is macroscopic.

The conclusion is that it doesn't matter much for the distribution of energies whether a subsystem is in equilibrium with a large subsystem or a small one – as long as they are macroscopic. This is consistent with general experience of measured temperatures and experimental confirmations of the zeroth law of thermodynamics.

The next step is to explore the consequences of Eqs. (29), (30), and (31) for the entropy through the use of a Massieu function.

III.3. Massieu functions

It is well known that the canonical partition function is related to the Helmholtz free energy, $F = U - TS$, by the equation

$$\ln Z(\beta, V, N) = -\beta F(T, V, N), \quad (33)$$

where T is the temperature, and $\beta = 1/k_B T$. The Helmholtz free energy is, of course, the Legendre transform of the fundamental relation $U = U(S, V, N)$ with respect to temperature, which we will denote as $F(T, V, N) = U[T]$, indicating the Legendre transform by the square brackets around the new variable T [26, 27].

Although the use of the thermodynamic potentials derived from the fundamental equation $U = U(S, V, N)$ through Legendre transforms are familiar to all students of thermodynamics, they are not appropriate for calculating the properties of non-monotonic entropy functions. The reason is that if $S = S(U, V, N)$ is not monotonic in U , the function cannot be inverted to find $U = U(S, V, N)$. However, we can still use Massieu functions, which are Legendre transforms of $S = S(U, V, N)$ [26, 27]. It will be particularly useful to define a dimensionless entropy, $\tilde{S} = S/k_B$, in forming Massieu functions.

From the differential form of the fundamental relation for dS , we can see that

$$d\tilde{S} = \beta dU + \beta P dV - \beta \mu dN, \quad (34)$$

where P is the pressure, V is the volume, μ is the chemical potential, and N is the number of particles. The inverse temperature β is found from the usual equation, which can be written as

$$\beta = \left(\frac{\partial \tilde{S}}{\partial U} \right)_{V, N}. \quad (35)$$

The Legendre transform (Massieu function) is given by

$$\tilde{S}[\beta] = \tilde{S} - \beta U = -\beta (U - TS) = -\beta F, \quad (36)$$

so that

$$\tilde{S}[\beta] = \ln Z(\beta, V, N). \quad (37)$$

The differential form of the Massieu function $\tilde{S}[\beta]$ is then

$$d\tilde{S}[\beta] = -U d\beta + \beta P dV - \beta \mu dN. \quad (38)$$

This immediately gives us

$$\left(\frac{\partial \tilde{S}[\beta]}{\partial \beta} \right)_{V, N} = -U = - \left(\frac{\partial (\beta F)}{\partial \beta} \right)_{V, N}, \quad (39)$$

where the last equality is a well-known thermodynamic identity[26, 27].

III.4. Inverse Legendre transform of $\tilde{S}[\beta]$ to find $S(U)$

To carry out the inverse Legendre transform of $\tilde{S}[\beta]$ to find $S(U)$, use Eq. (39) to find $U = U(\beta)$. Since U is a monotonic function of β , even for a non-monotonic density of states, we can invert this equation to obtain $\beta = \beta(U)$. From Eq. (35), we can find

$$\tilde{S} = \tilde{S}[\beta] + \beta(U)U. \quad (40)$$

Finally, the entropy with the usual dimensions is given by

$$S = k_B \tilde{S}. \quad (41)$$

III.5. Alternative calculation of the entropy $S(U)$ from $\beta = \beta(U)$

Since $\beta = \beta(U)$ was found by inverting $U = U(\beta)$, the entropy can also be calculated by integrating the thermodynamic identity in Eq. (35) to find

$$S = k_B \int_{U_{min}}^U \beta(U') dU' \quad (42)$$

where U_{min} is the minimum value of the thermodynamic energy U . Both methods produce the same results.

The next section discusses the application of these methods to calculate $S(U)$ for either a monotonic entropy or a non-monotonic entropy.

IV. EXAMPLES OF THE ENTROPY OF QUANTUM SYSTEMS

This section contains explicit calculations of the entropy of quantum systems, as illustrations of the methods described in the previous section. The first example is a system of quantum simple harmonic oscillators, which has a monotonic dependence of the entropy as a function of energy. . The second example is a system composed of two-level objects. This system has a non-monotonic entropy and illustrates how negative temperatures can arise in a quantum system. For completeness, I will discuss two kinds of two-level systems.

A clear distinction should be made between macroscopic systems composed of microscopic objects (simple harmonic oscillators, two-level objects, etc.), as discussed in this section, and the composite systems discussed in Sections II and III, which were composed of macroscopic subsystems.

IV.1. A system composed of quantum simple harmonic oscillators

Consider a system composed of N simple harmonic oscillators. For simplicity, we will assume that the frequencies of all oscillators are the same, so that the Hamiltonian is

$$H_{SHO,k} = \hbar\omega(n_k + 1/2), \quad (43)$$

where \hbar is Planck's constant, ω is the angular frequency, and $n_k = 0, 1, 2, \dots$. The partition function of the complete system of N oscillators is well known to be

$$Z_{SHO} = \exp(-\beta\hbar\omega N/2) (1 - \exp(-\beta\hbar\omega))^{-N}, \quad (44)$$

so that

$$\begin{aligned} \tilde{S}_{SHO}[\beta] &= \ln Z_{SHO} \\ &= -\frac{1}{2}N\beta\hbar\omega - N \ln(1 - \exp(-\beta\hbar\omega)) \end{aligned} \quad (45)$$

The energy is given by the negative partial derivative of $\tilde{S}_{SHO}[\beta]$ with respect to β , as in Eq. (39).

$$U_{SHO} = \frac{1}{2}\hbar\omega N + N\hbar\omega (\exp(\beta\hbar\omega) - 1)^{-1} \quad (46)$$

IV.1.1. Finding S_{SHO} by Legendre transform

To make the following equations more compact, define

$$\hat{U}_{SHO} = U_{SHO} - \frac{1}{2}\hbar\omega N. \quad (47)$$

The next step is to invert $\hat{U}_{SHO} = \hat{U}_{SHO}(\beta)$, to find $\beta = \beta(\hat{U}_{SHO})$. To make the notation still more compact, we will express the results in terms of a dimensionless energy variable

$$x = \hat{U}_{SHO}/N\hbar\omega = \frac{U_{SHO} - \frac{1}{2}\hbar\omega N}{N\hbar\omega}, \quad (48)$$

which gives

$$\beta = \frac{1}{\hbar\omega} \ln[1/x + 1] = \frac{1}{\hbar\omega} \ln\left[\frac{1+x}{x}\right] \quad (49)$$

The inverse Legendre transform, $\tilde{S}_{SHO}[\beta]$ as a function of x is

$$\tilde{S}_{SHO}[\beta] = -\frac{1}{2}N \ln[1/x + 1] + N \ln(1 + x). \quad (50)$$

Using Eq. (40), the dimensionless entropy is found to be

$$S_{\text{SHO}} = k_B \tilde{S}_{\text{SHO}} = N k_B [-x \ln x + (1+x) \ln(1+x)] \quad (51)$$

It is readily confirmed that the same result is obtained by numerical integration of the inverse temperature.

In the limit of $\beta \rightarrow \infty$ (or $T \rightarrow 0$) the energy goes to its minimum value, $U_{\text{SHO}} \rightarrow \hbar\omega N/2$, and $x \rightarrow 0$. In this limit, $S_{\text{SHO}} \rightarrow 0$, as expected from the third law of thermodynamics (Nernst theorem).

IV.2. A system of two-level quantum objects

The next example illustrates the thermodynamics of a system with a bounded energy spectrum and a non-monotonic entropy. This system displays negative temperatures.

Consider a collection of N two-level quantum objects,

$$H_{2\text{-level}} = \epsilon \sum_{k=1}^N n_k, \quad (52)$$

where ϵ is the energy difference between the two levels in each object, and $n_k = 0$ or 1 . The partition function $Z_{2\text{-level}}$ can be found by standard methods.

$$Z_{2\text{-level}} = [1 + \exp(-\beta\epsilon)]^N \quad (53)$$

This gives

$$\tilde{S}_{2\text{-level}}[\beta] = \ln Z_{2\text{-level}} = N \ln [1 + \exp(-\beta\epsilon)], \quad (54)$$

and, using Eq. (39),

$$U_{2\text{-level}} = N\epsilon (\exp(\beta\epsilon) + 1)^{-1}. \quad (55)$$

IV.2.1. Finding $S_{2\text{-level}}(U)$ by Legendre transform

As before, we simplify the notation by defining a dimensionless energy

$$y = \frac{U_{2\text{-level}}}{N\epsilon}. \quad (56)$$

The same type of calculation used for the simple harmonic oscillators gives the inverse temperature as

$$\beta = \frac{1}{\epsilon} \ln \left[\frac{1}{y} - 1 \right] = \frac{1}{\epsilon} \ln \left[\frac{1-y}{y} \right]. \quad (57)$$

A little algebra then gives

$$S_{2\text{-level}} = -Nk_B [y \ln y + (1 - y) \ln(1 - y)] \quad (58)$$

As was the case for the system composed of simple harmonic oscillators, integration of the inverse temperature produces the same result as the Legendre transform.

$S_{2\text{-level}}$ has positive temperatures for $y < 0.5$, and negative temperatures for $y > 0.5$, as expected. The entropy is symmetric for $y \leftrightarrow 1 - y$. The entropy goes to zero in the limits $y \rightarrow 0$ and $y \rightarrow 1$, also as expected.

IV.3. Independent Ising spins

Since a system composed of non-interacting Ising spins is isomorphic to the two-level system discussed above, its entropy can be obtained with little effort.

Consider the Hamiltonian

$$H_{\text{spins}} = -b \sum_{j=1}^N \sigma_j, \quad (59)$$

where σ_j takes on the values $+1$ and -1 , and the parameter b represents an applied magnetic field. The mapping between the variable n_j , which take on the values 0 and 1, and the spins is

$$\sigma_j = 2n_j - 1, \quad (60)$$

and the energies map as

$$\frac{U_{2\text{-level}}}{N\epsilon} = \frac{U_{\text{spins}}}{2Nb} + \frac{1}{2}. \quad (61)$$

Defining a dimensionless energy for the spin system by

$$r = \frac{U_{\text{spins}}}{Nb}, \quad (62)$$

Eq. (61) becomes

$$y = \frac{r + 1}{2}, \quad (63)$$

where y is the dimensionless energy for the two-level system defined in Eq. (56). This gives the entropy of the spin system as

$$S_{\text{spins}} = -\frac{Nk_B}{2} [(1 - r) \ln(1 - r) + (1 + r) \ln(1 + r) - 2 \ln 2]. \quad (64)$$

S_{spins} has positive temperatures for $r < 0$, and negative temperatures for $r > 0$, as expected, with an obvious symmetry for $r \leftrightarrow -r$. The entropy goes to zero in the limits $r \rightarrow -1$ and $r \rightarrow +1$, also as expected.

A slight modification of the derivations given above would also allow the calculation of the entropy of a system composed of two-level systems or simple harmonic oscillators with arbitrary distributions of energy-level spacings.

Now that these examples of derivations of the entropy of quantum systems are complete, they can be tested against exact results and compared with the predictions of the volume entropy advocated by opponents of the concept of negative temperatures.

V. COMPARISON OF $S_{\text{2-level}}$ WITH THE VOLUME ENTROPY

Comparisons with the volume entropy as used by its advocates are somewhat ambiguous because they present their ideas in terms of a non-analytic expression for the entropy of a quantum system[1, 4]. However, their basic claim is that the logarithm of the integral of the density of states gives the true entropy, which always has positive temperatures. The volume entropy is calculated in the next section using the same procedure used in Ref. 4. The predictions of the volume entropy are then tested against exact results and compared with the expressions of the entropy derived in Section IV.

V.1. Calculation of the volume entropy for a system composed of two-level objects

In the notation of Ref. 4, $\tilde{S}_{\text{2-level}}$ is related to the density of states $\omega(y)$ by

$$\begin{aligned}\tilde{S}_{\text{2-level}} &= \ln \omega(y) \\ &= -N [y \ln y + (1 - y) \ln(1 - y)],\end{aligned}\tag{65}$$

where the explicit dependence on the dimensionless energy y is taken from Eq. (58). Since the dimensionless entropy is being expressed in terms of a dimensionless energy variable, $y = U_{\text{2-level}}/N\epsilon$, there is no need for the energy parameter that Ref. 4 included in the logarithm.

The dimensionless volume entropy is given by

$$\tilde{S}_G(y) = \ln \Omega(y),\tag{66}$$

where

$$\begin{aligned}\Omega(y) &= \int_0^y \omega(y') dy' \\ &= \int_0^y (1-y')^{-N(1-y')}(y')^{-Ny'} dy'.\end{aligned}\tag{67}$$

Carrying out the integral in Eq. (67) (numerically) gives \tilde{S}_G . After this is done, the fact that

$$\omega(y) = \frac{\partial \Omega(y)}{\partial y}\tag{68}$$

gives a simple expression for the inverse temperature.

$$\beta_G = \frac{\partial \tilde{S}_G(y)}{\partial y} = \frac{\omega(y)}{\Omega(y)}\tag{69}$$

These explicit expressions for the volume entropy and its associated temperature are tested against exact results in the next subsection.

V.2. Comparison between predictions of the partition of energy between subsystems in equilibrium for different entropies

Consider thermal equilibrium between two two-level subsystems with the same level spacing ϵ , but differing in size by a factor of f . Subsystem 1 contains fN two-level objects, and subsystem 2 is $1/f$ smaller, with N objects. Even without calculations, it is obvious that equipartition of energy between the two subsystems in equilibrium requires

$$\frac{U_1}{fN} = \frac{U_2}{N}.\tag{70}$$

The prediction of $\tilde{S}_{2\text{-level}}$ comes from setting the temperatures equal. Using Eq. (57),

$$\beta_j = \frac{1}{\epsilon} \ln \left[\frac{f_j N \epsilon}{U_{2\text{-level},j}} - 1 \right] = \frac{1}{\epsilon} \ln \left[\frac{1}{y_j} - 1 \right],\tag{71}$$

for $j = 1$ or $j = 2$, and $f_1 = f$, while $f_2 = 1$. Since ϵ is the same in both subsystems, it is clear that the condition of equilibrium is $y_1 = y_2$, which is equivalent to Eq. (70). This confirms that $\tilde{S}_{2\text{-level}}$ correctly predicts equipartition for these subsystems with non-monotonic $\omega(y)$.

The numerical computations for the equilibrium predictions of the volume entropy have been carried out for test cases and plotted in Fig. 1. For comparison, the exact condition for equilibrium, which is a straight line given by Eq. (70), is also shown. This exact equilibrium condition is identical to that predicted by $S_{2\text{-level}}$, as derived in Section

IV.2. For values of the energy less than half the maximum energy, all predictions are in good agreement with the equipartition of energy. However, for values of the energy more than half the maximum energy, the predictions of the volume entropy deviate significantly from the correct equilibrium conditions.

The origin of the errors made by the volume entropy can be traced back to the size dependence of the temperature T_G given by the volume entropy: the larger the subsystem, the higher T_G . Since subsystem 1 is larger than subsystem 2, it also has a higher value of T_G at equilibrium than subsystem 2. Equal values of T_G in the two subsystems can only be achieved if subsystem 2 has a higher energy than appropriate for equilibrium, leading to the erroneous predictions of the volume entropy shown in Fig. 1.

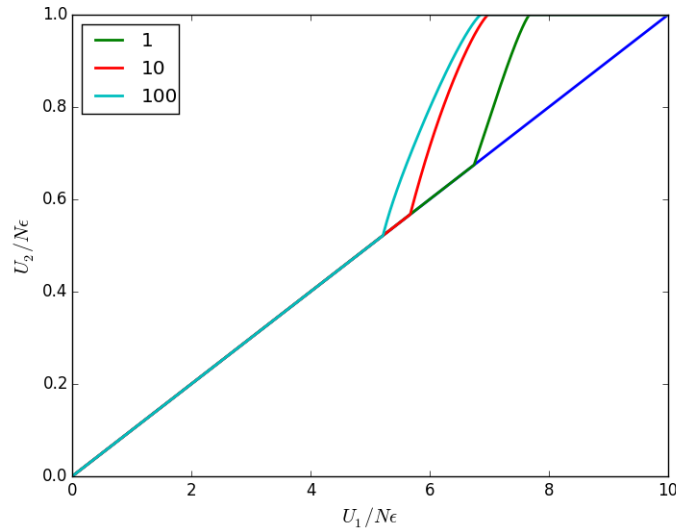


FIG. 1. Plot of the predictions of the volume entropy are compared with those of the entropy given by $S_{2\text{-level}}$ in Eq. (58) for the distribution of energy between two subsystems of two-level objects in thermal equilibrium. The exact condition of equipartition of energy is indicated by the straight line, which is also the prediction of $S_{2\text{-level}}$. The three curves giving the volume entropy predictions are for subsystem sizes $[N_1, N_2]$ of $[10, 1]$, $[100, 10]$, and $[1000, 100]$. In each case, the value of N_2 is given in the legend. Larger deviations of the curves for the volume entropy from the exact results correspond to larger subsystems. Increasing the ratio of the subsystem sizes also increases the violation of equipartition of energy.

VI. CONCLUSIONS

I have demonstrated that the entropy of a macroscopic quantum system is a continuous function of the thermodynamic energy, as opposed to the step functions and delta functions proposed by other authors[1, 4, 6, 24, 25].

The expressions for the entropy of simple harmonic oscillators in Eq. (51) and two-level systems in Eqs. (58) and (64) satisfy the postulates of thermodynamics. They are fundamental thermodynamic relations that completely characterize the correct thermodynamic properties of these systems. Because the fundamental relation of a thermodynamic system can be shown to be unique, any valid definition of the entropy of macroscopic quantum systems must be equivalent to the one presented in this paper.

An interesting feature of the definition of entropy presented here is that subsystems with incommensurate energy eigenvalues can be in equilibrium with each other. It is, of course, well known experimentally that differences in microscopic energy-level spacings do not prevent equilibration, but this fact has not been obvious from earlier proposed expressions for the entropy of macroscopic systems.

Finally, I have shown that the entropy of two-level objects confirms the validity of the concept of negative temperatures.

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